

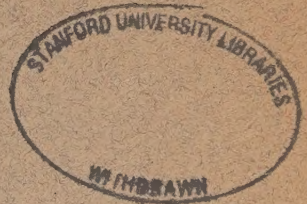
The Action of Potassium Hydroxide on Dihydroxy Acetone

DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE
SCHOOL OF THE OHIO STATE UNIVERSITY

BY

WILLIAM ROBERT CORNTHWAITE



The Ohio State University
1928

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ACKNOWLEDGMENT

I desire to express my great appreciation to Professor William Lloyd Evans for his constant enthusiasm, help and suggestions during the pursuance of this work.

Further I wish to extend my thanks to Dr. Marion Hollingsworth for the use of certain equipment from the Division of Quantitative Analysis.

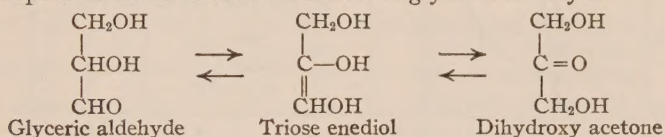
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THE ACTION OF POTASSIUM HYDROXIDE ON DIHYDROXY ACETONE

The studies of Hass and Evans¹ on the behavior of crystalline glyceric aldehyde in potassium hydroxide solutions, in which the concentration of the base varied from 0.2 to 6 *N* at 25 and 50°, showed that the amounts of the products obtained under the variable conditions employed were dependent on both the temperature and the normality of the alkali used. Pyruvic aldehyde, lactic, acetic and formic acids were the reaction products studied in the work on glyceric aldehyde. It was pointed out² that solutions of glyceric aldehyde³ in the presence of potassium hydroxide should form an equilibrated system in the same manner as that which Lobry de Bruyn and Alberda van Ekenstein found existed in alkaline solutions of *d*-glucose and *d*-galactose. Furthermore, the active component of such a solution should be an enediol or its dissociation products similar to the systems postulated by Nef and his collaborators in the case of certain hexoses.

If these views are correct then it is clear that the following reaction represents the equilibrated condition existing between the three carbon atom compounds in an alkaline solution of glyceric aldehyde.



On the basis of this discussion it is expected that dihydroxy acetone should react in aqueous solutions of potassium hydroxide in the same general manner that glyceric aldehyde does. To determine this point was one of the principal objects of these experiments by reason of the importance of dihydroxy acetone in carbohydrate chemistry, especially in its structural relation to fructose.

Experimental Part

Reagents.—The potassium hydroxide, alcohol, phenylhydrazine, zinc carbonate, phosphoric and hydrochloric acids were of the same degree of purity as those used in the work on glyceric aldehyde. The dihydroxy acetone was purchased under the name of "Oxantin." Before using, it was kept in a vacuum desiccator over soda lime and calcium chloride for at least one week. It melted at 78–79° (corr.).⁴

¹ Evans and Hass, *J. Am. Chem. Soc.*, **48**, 2703 (1926).

² Ref. 1, p. 2709.

³ Wohl and Neuberg, *Ber.*, **33**, 3110 (1900).

⁴ Bertrand, *Ann. chim.*, [8] **3**, 255 (1904); Piloty, *Ber.*, **30**, 3165 (1898).

Procedure.—In order that my data might be comparable with those obtained from the action of aqueous solutions of potassium hydroxide on glyceric aldehyde, every experimental detail of the work recorded in this report was an exact duplicate of that employed in the study of glyceric aldehyde, save that dihydroxy acetone was used instead of the aldehyde.

Products of the Reaction.—At various stages qualitative examination of my reaction mixtures was made for pyruvic aldehyde, acetol, lactic, acetic and formic acids.

Data.—My quantitative data are shown in Figs. 1, 2, 3, 4, 5 and 6. For the sake of comparison the data by Evans and Hass from glyceric aldehyde are shown in the drawings by means of dotted lines.

Theoretical Part

The results obtained in these experiments were found to be in complete qualitative agreement with those obtained by the action of aqueous solutions of potassium hydroxide on glyceric aldehyde. The suggestions

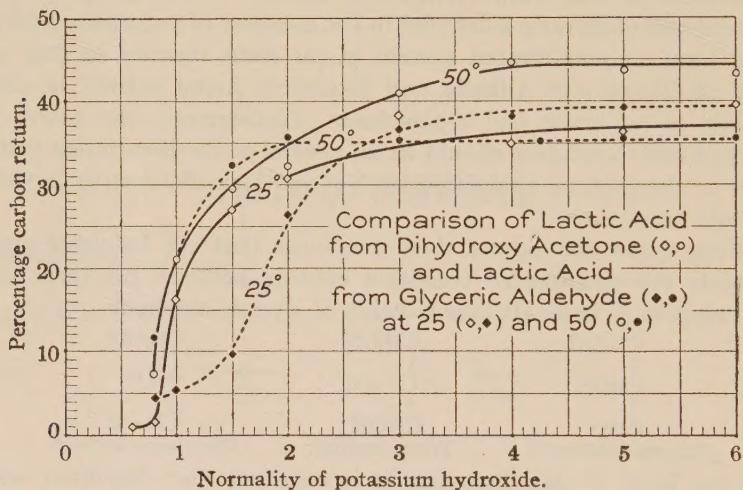
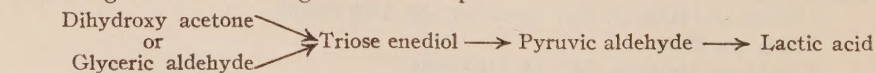


Fig. 1.

offered for the reaction mechanism involved in the formation of pyruvic aldehyde, lactic, acetic and formic acids from glyceric aldehyde are in accord with the data obtained by me in these experiments with dihydroxy acetone under precisely similar conditions. In addition to the discussion previously given concerning the general reaction involved in the formation of the above compounds, I wish to supplement it with the following brief statements with reference to my own data.

Lactic Acid.—If dihydroxy acetone and glyceric aldehyde form one and the same triose enediol, then it follows that lactic acid may be formed according to the following series of steps:⁵



⁵ Ref. 1, p. 2710; compare Neuberg, *Biochem. Z.*, 71, 250 (1915).

The molecular mechanism of this series of changes may be regarded as an application of the suggestion offered by Miss Marjorie Pickard Benoy and Evans⁶ for the formation of saccharinic acid lactones from the enediols of glucose and galactose. The comparative yields of lactic acid from the two trioses are shown in Fig. 1. No lactic acid (zinc lactate)

PLATE I
QUANTITATIVE DATA FOR DIHYDROXY ACETONE AT 25°

Alkali Normality	Per cent. carbon return for acetic acid	Per cent. carbon return for formic acid	Per cent. carbon return for lactic acid
0.2 <i>N</i>	1.05	0.54	None
.4 <i>N</i>	1.38	.68	None
.6 <i>N</i>	1.91	1.18	0.87
.8 <i>N</i>	1.88	1.22	1.88
1.0 <i>N</i>	1.67	1.32	16.36
1.5 <i>N</i>	1.61	1.61-0.82	27.01
2.0 <i>N</i>	1.55	2.25	30.75
3.0 <i>N</i>	1.49	2.39	38.64
4.0 <i>N</i>	1.17	1.94-1.49	35.02
5.0 <i>N</i>	1.17	1.39-1.76	36.47
6.0 <i>N</i>	1.32	1.33	39.80

was found at 25° in potassium hydroxide solutions at either 0.2 or 0.4 *N*, but appreciable amounts were present at 0.6 *N*. It is clear from the graph of my data that my quantitative results are also in general agreement

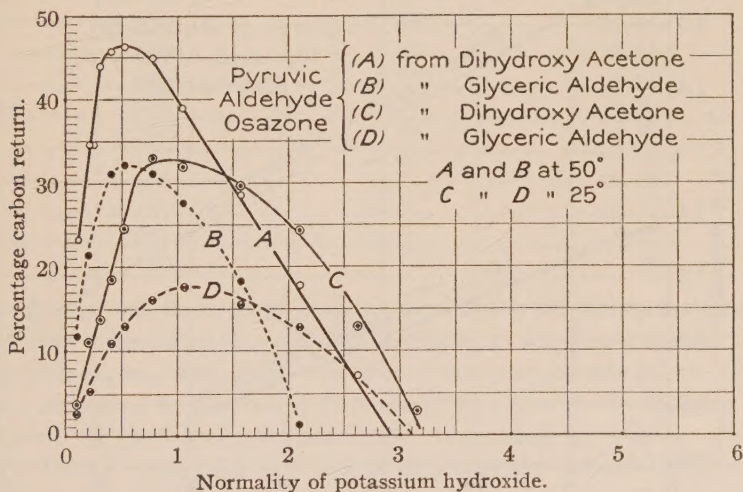


Fig. 2.

with the assumption that the lactic acid formation from glyceric aldehyde and dihydroxy acetone is following the same course.

Pyruvic Aldehyde.—The percentage of dihydroxy acetone carbon

⁶ Evans, Edgar and Hoff, *J. Am. Chem. Soc.*, **48**, 2675 (1926).

obtained as pyruvic aldehyde is shown in Fig. 2. The data obtained from glyceric aldehyde are also given with certain correction factors applied which were previously omitted.⁷ An examination of these curves

PLATE II

QUANTITATIVE DATA FOR DIHYDROXY ACETONE FOR 50°

Alkali normality	Per cent. carbon return for acetic acid	Per cent. carbon return for formic acid	Per cent. carbon return for lactic acid
0.2 N	2.37	0.82	None
.4 N	4.29	1.44	None
.6 N	5.17	2.26	None
.8 N	4.07	2.37	7.29
1.0 N	2.84	2.09	21.09
1.5 N	2.00	1.65	29.38
2.0 N	1.58	1.36	32.15
3.0 N	1.16	1.16	41.07
4.0 N	1.06	0.94	44.77
5.0 N	1.07	1.07	43.84
6.0 N	1.26	1.05	43.19

shows in a very clear way the effect of temperature on the reaction by reason of the fact that the maximum yield of pyruvic aldehyde from both of these trioses occurs at a lower normality at 50° in each case than it does

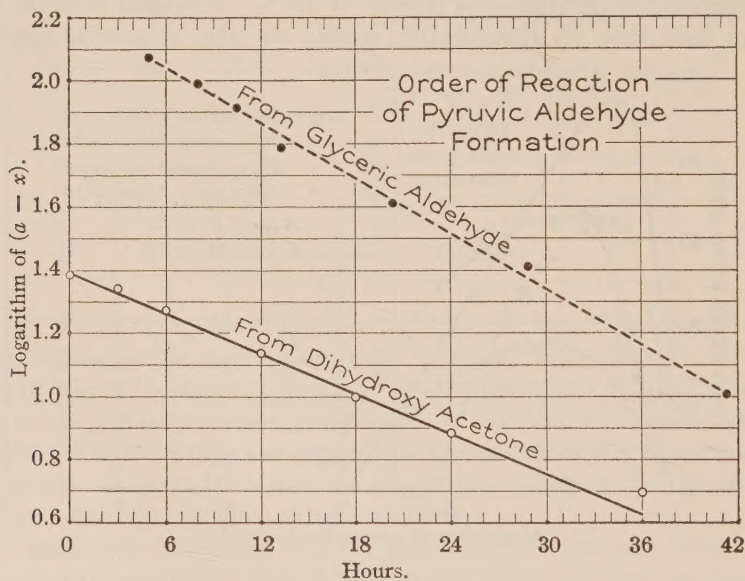


Fig. 3.

at 25°. Furthermore, it should be noted that the maximum yield of pyruvic aldehyde osazone from both compounds occurs at approximately

⁷ See Ref. 1, p. 2710.

the same normality for a given temperature. The fact that the maximum production of pyruvic aldehyde in dihydroxy acetone and glyceric aldehyde solutions occurs at practically the same alkali normality and that the general effect of temperature is also the same in each case, point very strongly to the assumption made above that a common intermediate compound, namely, the triose enediol, is formed in each case. Furthermore, the differences obtained in the yields of pyruvic aldehyde osazone from these two trioses at any given alkalinity under these experimental conditions seem to indicate that a condition exists in alkaline solution of these two carbohydrates similar to that observed by de Bruyn and van Ekenstein in alkaline solutions of glucose, mannose and fructose, that is, an equilibrated system in which the ratio of the amounts of the components present varied with the hexose used. It has been shown in this Laboratory⁸ that the oxalic acid-carbon dioxide ratio obtained in the oxidation of these three well-known hexoses in strongly alkaline solutions of potassium permanganate tends toward the same value as the temperature and normality of the alkali are increased.

PLATE III
PERCENTAGE CARBON RETURN METHYLGLYOXAL OSAZONE FROM DIHYDROXY
ACETONE

Normality of solution	25°	50°
0.1053	3.88	23.63
.2105	11.22	24.61
.3158	13.84	44.17
.4210	18.76	45.87
.5263	24.82	46.69
.7894	33.03	45.19
1.053	32.12	39.08
1.579	29.71	28.80
2.105	24.51	18.71
2.631	13.10	0.00
3.158	3.04	.00

If alkaline solutions of glyceric aldehyde and dihydroxy acetone form a common triose enediol as an intermediate in the formation of pyruvic aldehyde osazone, and if the amounts of the components in the solutions varied according to the triose used, then the order of the reaction in the formation of the aldehyde from both compounds at a given alkalinity should be the same and the rate of the reaction should be different in each case. In Fig. 3 this is shown to be the case, that is, the reaction is monomolecular. The temperature used was 25°. The bearing of the recent experiments of Fischer, Taube and Baer⁹ on the interpretation of my experimental data is very important. These investigators have

⁸ Evans, Buehler, Looker, Crawford and Holl, *J. Am. Chem. Soc.*, **47**, 3085 (1925).

⁹ Fischer, Taube and Baer, *Ber.*, **60B**, 479-485 (1927).

shown that crystalline glyceric aldehyde may be converted into dihydroxy acetone in boiling pyridine to the extent of 49%.³

In the work on glyceric aldehyde the view was expressed that acetic and formic acids resulted from a dissociation of pyruvic aldehyde into acetaldehyde and carbon monoxide. These two acids increase in amount

PLATE IV
ORDER OF REACTION DIHYDROXY ACETONE AND POTASSIUM HYDROXIDE AT 25°

Time, hrs.	Alkali normality	Grams osazone produced (total)	(A-x) in centigrams	Log of (A-x)
0	0.9891 <i>N</i>	0.0000	24.391	1.3872
3	.9891 <i>N</i>	.2508	21.88	1.3401
6	.9891 <i>N</i>	.5679	18.71	1.2710
12	.9891 <i>N</i>	1.0346	14.05	1.1476
18	.9891 <i>N</i>	1.3692	10.25	1.0107
24	.9891 <i>N</i>	1.6151	7.80	0.8921
36	.9891 <i>N</i>	1.9195	5.20	.7160
48	.9891 <i>N</i>	1.9714	4.68	.6702
96	.9891 <i>N</i>	2.4391	0.00	

with the alkalinity until a maximum has been reached, after which their amounts diminish due to the fact that the pyruvic aldehyde at that point is now being converted into lactic acid at a speed which increases with the alkalinity. This inter-relation of the formation of lactic, acetic and formic

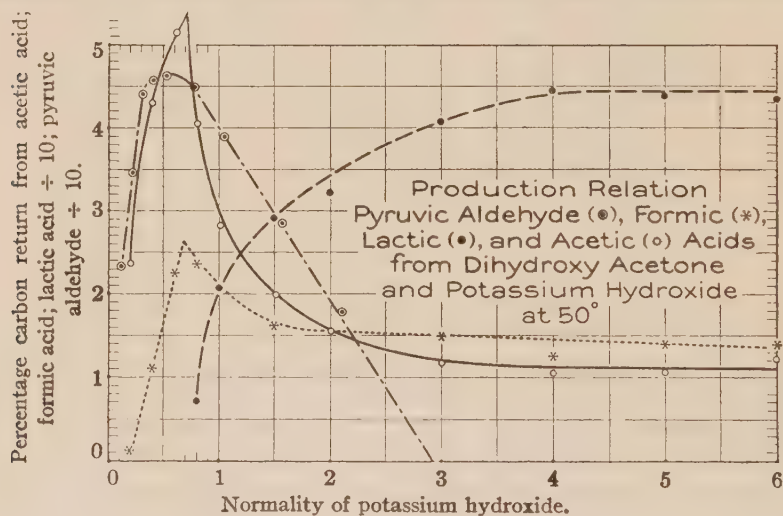


Fig. 4.

acids to the pyruvic aldehyde involved in the reaction of an aqueous solution of potassium hydroxide on dihydroxy acetone is clearly seen in Fig. 4. According to my experimental methods of measurement, the maximum yield for pyruvic aldehyde, acetic and formic acids and the minimum yield for lactic acid occur at approximately the same point of

alkalinity. The maximum yield of dihydroxy acetone carbon as pyruvic aldehyde is approximately the same as the maximum for that of lactic acid. The formic and acetic acid yields are given in Figs. 5 and 6, re-

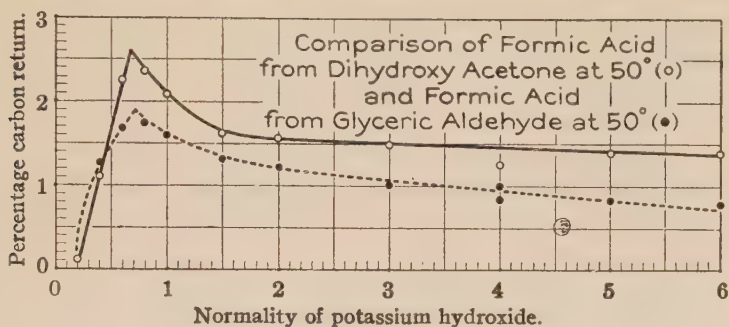


Fig. 5.

spectively. The differences in the yields of these two acids from the two sources are not very great. It is also conceivable that the triose enediol of these reactions may undergo dissociation into the active forms of glycolic and formaldehydes, which in turn may react to yield other substances, among which would be formic acid. My reaction mixtures were

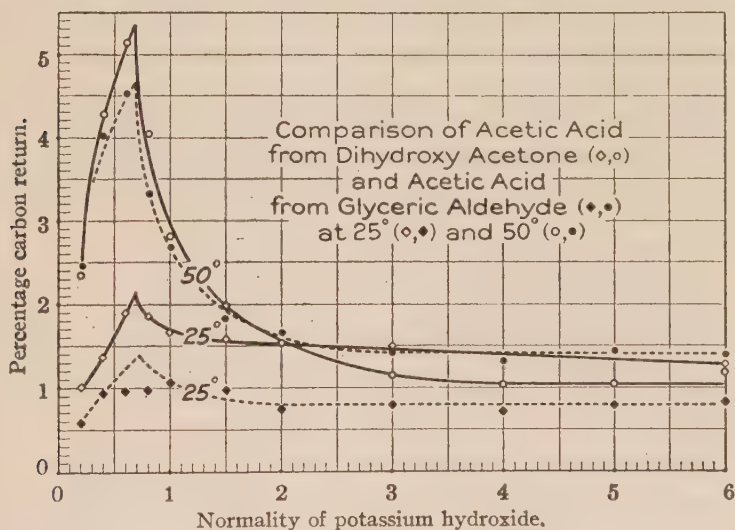


Fig. 6.

not examined for either glycol or glycolic acid. The view that a 1,2-enediol may undergo such a dissociation with subsequent chemical change has received much support in the recent experiments of Gustus and Lewis¹⁰

¹⁰ Gustus and Lewis, *J. Am. Chem. Soc.*, **49**, 1512 (1927); see also Baly, *The Rice Institute Pamphlet*, **12**, 93 (1925).

on the action of alkaline hydrogen peroxide solution on 2,3,4,6-tetra-methyl-*D*-glucose.

Summary

1. Molar solutions of dihydroxy acetone were treated with various concentrations of potassium hydroxide from 0.2–6 *N* at 25 and 50°. The resulting acetic, formic and lactic acids were measured quantitatively (Figs. 1, 5 and 6).

2. The yields of formic and acetic acids at 50° increased with the increasing alkali concentration until a maximum point was reached, after which they diminished. The same effect was observed for acetic acid at 25°.

3. Molar solutions of dihydroxy acetone were treated with alcoholic phenylhydrazine solutions in the presence of various concentrations of alkali. The yield of pyruvic aldehyde osazone increased with the alkalinity to a maximum at both 25 and 50°, after which it diminished. Increasing temperature increased the yield of the osazone (Fig. 2).

4. The maximum yield of pyruvic aldehyde osazone from both trioses occurs at the same alkali normality for a given temperature. This maximum is attained at a lower alkali normality at 50° than at 25°.

5. The yields of lactic acid at 25 and 50° increased to a constant maximum with both the increasing alkalinity and temperature. The maximum point is practically the same as that for the pyruvic aldehyde at these temperatures.

6. The data obtained are shown graphically in comparison with a similar study on glyceric aldehyde. The results seem to indicate that both dihydroxy acetone and glyceric aldehyde in alkaline solutions form systems similar to those observed by de Bruyn and van Ekenstein in alkaline solutions of the hexoses.

7. The differences observed in the yields of pyruvic aldehyde osazone are thought to be due to the differences in the equilibrium existing between glyceric aldehyde, dihydroxy acetone and triose enediol in alkaline solutions. This point of view is supported by the fact that the order of the reaction is the same in both cases, while the rate of the reaction is different (Fig. 3).

8. Since both trioses are thought to form one and the same enediol, then the lactic acid must be derived from the pyruvic aldehyde arising from this common enediol. The acetic and formic acids are thought to be derived from a dissociation of pyruvic aldehyde into acetaldehyde and carbon monoxide. The minimum point for lactic acid yields is therefore related to the maximum yields for pyruvic aldehyde, acetic and formic acids. This inter-relation is shown in Fig. 4.

AUTOBIOGRAPHY

I, William Robert Cornthwaite, was born in Elwood, Indiana, November 5, 1902. My elementary education was obtained in the Public Schools of Cassopolis, Michigan. In 1919, I was graduated from the Cambridge City, Indiana High School after three years of attendance. A Rector Scholarship was held by me at the De Pauw University, from which institution I received the degree of Bachelor of Arts in 1923. Since that time I have been in attendance at the Ohio State University as student, Graduate Assistant and Assistant, receiving the degree of Master of Arts in 1925.

